"On the Action of Radium Emanations on Diamond." By Sir WILLIAM CROOKES, F.R.S. Received June 9,—Read June 16, 1904.

When diamonds are exposed to the impact of radiant matter in a high vacuum they phosphoresce of different hues, and assume a dark colour, becoming almost black when the bombardment is long continued.\*

Some diamonds blacken in the course of a few minutes, while others require an hour or more to discolour.† This blackening is only superficial, and although no ordinary means of cleaning will remove the discoloration, it goes at once when the stone is polished with diamond powder. The fact that the black stain is not affected by ordinary oxidising reagents would seem to show that it is not due to a layer of amorphous carbon; but it might be graphite, which is much more resistant to oxidation. Becquerel has shown that graphite is converted into graphitic oxide by long digestion in a warm mixture of potassium chlorate and strong nitric acid, while diamond—even in a very finely powdered state—is absolutely unaffected by the mixture.‡

Some forms of graphite dissolve in strong nitric acid; others require a mixture of highly concentrated nitric and potassium chlorate to dissolve them, and even with this intense oxidising agent some graphites resist longer than others. M. Moissan has shown that the power of resistance to nitric acid and potassium chlorate is in proportion to the temperature at which the graphite has been formed, and with reasonable certainty we can estimate this temperature by the resistance of the graphite to this reagent.

Judging from the long time required to remove the superficial darkening from diamond, the graphite is as resistant as that formed at the temperature of the electric arc.

On one occasion when I had blackened the surfaces of diamonds by molecular bombardment in vacuo M. Moissan was present, and took some away with him for further examination. He subsequently reported the results in the 'Comptes Rendus.'§ He heated the diamond to 60° in an oxidising mixture of potassium chlorate and fuming nitric acid prepared from mono-hydrated sulphuric acid and potassium nitrate fused and

- \* 'Phil. Trans.,' 1879, Part II, p. 658, par. 625.
- † At a lecture before the Royal Institution on June 11, 1897, I exposed a flat macle crystal of diamond to radiant matter bombardment before the audience for about 5 minutes, a strip of metal covering part of the stone. On removing the diamond from the vacuum tube and projecting its image on the screen with the electric lantern, the image of the darkening was very apparent.
  - ‡ 'Ann. de Chim. et de Phys.,' [4], vol. 19, p. 392.
  - § Vol. 124, No. 13.

quite free from moisture. The action on the black layer is very slow. There is produced graphitic oxide, which at an increased temperature yields pyrographitic acid, easily destroyed by nitric acid. Hence the variety of carbon which coated the diamond was graphite. The transformation of diamond into graphite requires the high temperature of the electric arc. The higher the temperature to which graphite is raised the greater is its resistance to oxidation. M. Moissan concludes that the temperature reached by the surface of the diamond in my radiant matter tubes is probably about 3600°.

The  $\beta$ -rays from radium having like properties to the cathode stream in a radiant matter tube, it was of interest to ascertain if they would exert a like difference on diamond. Two Bingara diamonds, A and B, weighing respectively 0.960 and 1.020 grains, were selected as near as the eye could judge of the same size and colour—very pale yellow, technically known as "off colour." Diamond A was put in a drawer far removed from radium or any radio-active body. Diamond B was kept close to a quartz tube containing about 15 milligrammes of pure radium bromide sealed in vacuo. It phosphoresced brightly and continued to glow the whole time of the experiment.

After a fortnight the two diamonds were put side by side and compared. I could see no appreciable difference in colour between them. Diamond B was now replaced close to the quartz tube of radium, and they were kept in contact for six weeks. At the end of that time examination again showed scarcely any difference between the two. The one which had been near the radium might be a little the darker of the two, but the difference was too slight to enable me to speak positively.

Diamond B was now put inside a tube with radium bromide, the salt touching it on all sides, as it was thought possible that a screen of quartz might interfere with the passage of emanations which would act on the diamond. The comparison diamond was kept removed from the emanations as before. The experiment was continued for 78 days, when the two diamonds were again examined. There was now a decided difference in colour between them; diamond A was of its original pale yellow "off colour," and diamond B was of a darker appearance and of a bluish-green tint, with no yellow colour apparent.

It thus appears that the property which radium emanations possess of darkening transparent bodies which they impinge upon—a property very marked in the case of glass, and less with quartz—also holds good in the case of diamond.

Diamond B was now heated to 50° C. in a mixture of strongest nitric acid and potassium chlorate for 10 days, the mixture being renewed each day. At the end of this time the diamond had lost its dull surface colour, and was as bright and transparent as the other stone, but its tint had changed from yellow to a pale blue-green.

The radium emanations have therefore a double action on the The  $\beta$ -rays (electrons) effect a superficial darkening, converting the surface into graphite in a manner similar to, but less strongly than, the more intense electrons in the cathode stream. But the alteration of the body colour of the stone by emanations which are obstructed by the thinnest film of solid matter, even by a piece of thin paper, is not so easy to understand. A superficial action might be expected, but not one penetrating through the whole thickness of the diamond. I believe the alteration of colour is a secondary effect; in presence of radium the diamond is extremely phosphorescent, and it continues to shine during the whole time of the experiment. This constant state of vibration in which the diamond was kept for many weeks may have caused an internal change revealing itself in a change of colour. Indeed, it is not difficult to suppose that a chemical as well as a physical action may result. If the yellow colour is due to iron in the ferric state a reduction to the ferrous state would quite account for the change of colour to a pale blue-green.

This alteration of colour may be of commercial importance. If "off colour" stones can be lightened their value will increase, while if the prolonged action of radium is to communicate to them a decided colour they would be worth much more as "fancy" stones.

[Added June 16, 1904.—After the 10 days' heating in the above acid mixture the two diamonds were put together in a glass tube and carried about for 25 days, sometimes loose and sometimes in the tube. They then were laid near together on a sensitive film in total darkness for 24 hours. On developing, diamond B had impressed a strong image on the film, but only a very faint mark could be seen where the other diamond had been. Probably this slight action was due to a little radio-activity induced in A during its 25 days' proximity to B.

The experiment was then repeated for confirmation, allowing the diamonds to remain on the sensitive surface for only 5 hours. On development, a good image of diamond B was seen, but not so black as in the former case.

The fact that diamond B was strongly radio-active after it had been away from radium for 35 days, for 10 of which it was being heated in a mixture powerful enough to dissolve off its outer skin of graphite, seems to me proof that radio-activity is by no means a simple phenomenon. It not merely consists in the adhesion of electrons or emanations, given off by radium, to the surface of an adjacent body, but the property is one involving deep-seated layers below the surface, and like the alteration of tint is probably closely connected with the intense phosphorescence the stone had been experiencing during its 78 days' burial in radium bromide.]

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